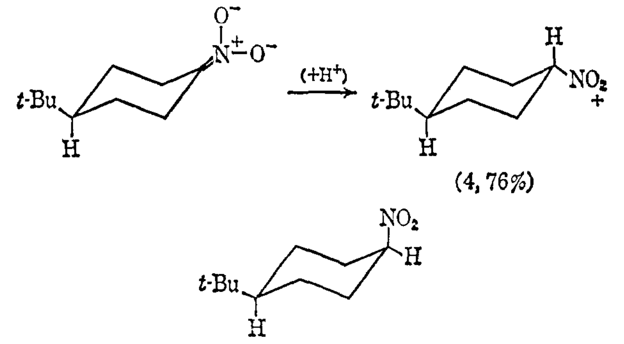
almost exclusively the *cis* isomer (equatorial α-proton, axial nitro group).[4] It was suggested that this might be due to the greater steric hindrance (by the C-3 and C-5 axial hydrogen atoms) for approach of the proton donor from the "axial side." The present results suggested that the effect might lie in the steric effect of the phenyl group rather than in the steric effect of the C-3 and C-5 axial hydrogen atoms. To test this point the nitronate ion derived from 4-*t*-butyl-1-nitrocyclohexane (**1** or **4**) was protonated by acidifying to a congo red end point with ethanolic sulfuric acid, then treating with acetic acid–sodium acetate and finally with water.[2,4] The product was a mixture of 4-*t*-butylcyclohexanone, **1**, and **4**. The ratio of ketone to nitroalkanes varied considerably, depending on the reaction conditions, but the ratio **1**:**4** was in each instance 1:3.[5]



(**4**, 76%)

(**1**, 24%)

It appears, therefore, that in the absence of hindering groups at C-2 there is but little preference for "axial" or "equatorial" approach of the proton donor. When a substituent is present at C-2 it must exert a sizable steric effect. This does not mean that the original suggestion of Zimmerman[4] must be abandoned,[6] but merely that it must be modified. It does appear likely, however, that the C-2 substituent is in an axial position in the transition state for nitronate ion protonation,[6] since it would exert a much greater steric effect from this position than from an equatorial position.[4]

Acknowledgment. This work was sponsored by the National Science Foundation (GP-4208).

(5) A. T. Nielsen, *J. Org. Chem.*, **27**, 2001 (1962), observed that protonation of the nitronate ion from 1,4-dinitrocyclohexane gave 55% *cis*- and 45% *trans*-1,4-dinitrocyclohexanes.

(6) S. K. Malhotra and F. Johnson, *J. Am. Chem. Soc.*, **87**, 5493 (1965).

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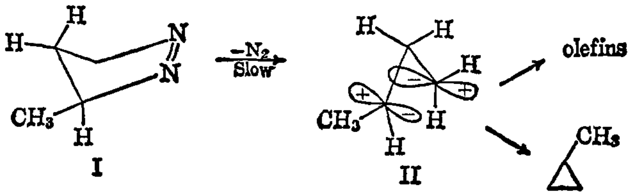
Thermolysis of *cis*- and *trans*-4-Deuterio-3-methyl-1-pyrazoline

Sir:

Thermolysis of simple alkyl-1-pyrazolines, in the gas phase, leads to a nitrogen-free intermediate.[1] On the basis of the olefin and cyclopropane products produced, structure II was proposed for the intermediate. We wish to report further evidence to support this structure.



I

II

The proposed intermediate (II) produced upon thermolysis of 3-methyl-1-pyrazoline (I) has a plane of symmetry through the four carbons. Such a structure has recently received theoretical support from extended Hückel molecular orbital calculations.[2] To test this symmetry we have prepared *cis*- and *trans*-4-deuterio-3-methyl-1-pyrazoline (III and IV), both being capable of producing the intermediate V. If V has a sufficient lifetime to become completely free of the nitrogen produced, then the product ratios will be independent of the initial stereochemistry. The intermediate V leads to predictions which are experimentally verifiable: (a) a 50:50 ratio of *cis*- and *trans*-2-deuteriomethylcyclopropane would be expected; (b) the yield of products, assuming a k_H/k_D ratio of 2.0 in the product-determining step,[1] should be that shown in Table I; (c) each olefin should exhibit the same k_H/k_D ratio irrespective of the initial source, III or IV.

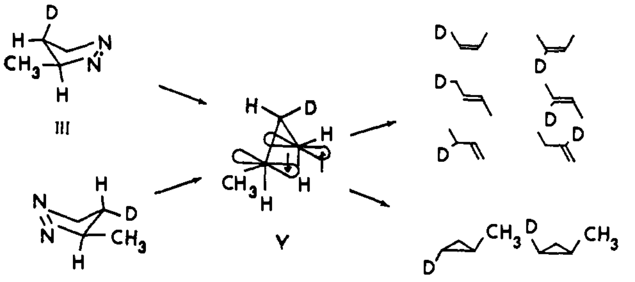
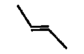


Table I. Product Proportions from the Pyrolysis of III and IV[a]

				
I, %	93.3 ± 0.6	1.9 ± 0.2	1.16 ± 0.12	3.7 ± 0.3
III and IV (predicted), %	94.9	1.4	0.9	2.8
III, %	95.1 ± 0.5	1.4 ± 0.2	1.0 ± 0.1	2.5 ± 0.3
IV, %	94.7 ± 0.5	1.5 ± 0.2	1.1 ± 0.2	2.7 ± 0.3

[a] Analysis carried out on a 20-ft column of silver nitrate and propanediol on Firebrick and a 20-ft column of dimethylsulfolane on Chromosorb.

The synthesis of III was achieved by the chlorination of *trans*-2-butene on a preparative scale using the procedure of Walling and Thaler.[3] Treatment of the *trans*-1-chloro-2-butene[4] with deuterium bromide in ether produced 3-bromo-1-chloro-2-deuteriobutane[5] which, upon treatment with hydrazine and oxidation of the

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(1) R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3963 (1966).

(2) R. Hoffmann, Abstracts, 151st National Meting of the American Chemical Society, Pittsburgh, Pa., March 1966, Paper 109K.

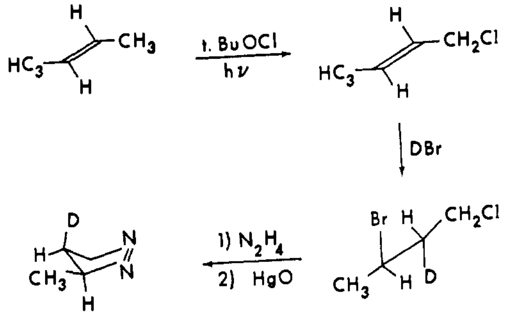
(3) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

(4) The *trans*-1-chloro-2-butene was separated from the 3-chloro-1-butene produced by preparative glpc using a 20-ft silicone oil on Fluoropak column.

(5) The procedure used was essentially that of H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).

resulting pyrazolidine with mercuric oxide,[6] produced a pyrazoline whose nmr spectrum (100 MHz) lacked the proton at τ 9.01. This signal was previously assigned[5] to the hydrogen on C_4 *cis* to the methyl group. The over-all sequence is indicated in Scheme I. The *trans* isomer IV was similarly produced from *cis*-2-butene and lacked the proton signal at τ 7.92.

Scheme I



The pyrazolines III and IV were pyrolyzed in a conditioned stainless-steel reactor at 218.0°[7] using an initial pressure of 100 torr. The hydrocarbon products were then separated by preparative gas chromatography.[8] Careful integration of the nmr spectrum of each of the olefins produced the data in Table II and allows one to calculate the mole per cent N_a of olefin produced by hydrogen migration *vs.* that produced by deuterium migration, N_b.

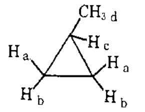
Table II. Nmr Analysis of Olefins Produced (Solvent $CDCl_3$)

Source		1-Butene	*cis*-2-Butene	*trans*-2-Butene
III	R^a	0.80 ± 0.02	4.4 ± 0.4	4.1 ± 0.5[c]
	% N_a	78	72	63
	% N_b	22	28	37
	k_H/k_D	3.5 ± 1.0	2.7 ± 1.0	1.7 ± 0.6
IV	R^a	0.78 ± 0.02	4.1 ± 0.4[b]	4.2 ± 0.4[b]
	% N_a	75	63	65
	% N_b	25	37	35
	k_H/k_D	3.0 ± 0.6	1.7 ± 0.6	1.9 ± 0.6

[a] R is the ratio of integrated areas of allylic to vinyl protons. [b] An impurity in the deuteriochloroform at τ 8.45 prevented a more accurate integration of the methyl signal. [c] Spectra run in carbon tetrachloride.

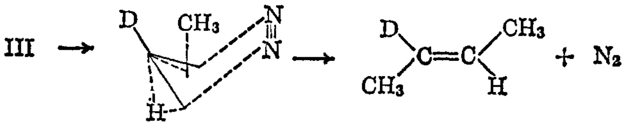
The nmr spectrum of methylcyclopropane in chloroform is as indicated in Table III. Integration of the spectrum of samples of methylcyclopropane derived from III and IV indicated an equimolar mixture of *cis*- and *trans*-2-deuteriomethylcyclopropane.

Table III. Nmr Analysis of Methylcyclopropane in $CDCl_3$ at 100 MHz ($CHCl_3$ Used as Internal Standard)

	Proton	τ	Known	Integrated areas[a] From III	Integrated areas[a] From IV
	H_a H_b H_c H_d	10.06 9.60 9.35 9.02	2.00 2.02 0.99 3.00	1.51 1.49 1.00 3.00	1.51 1.49 1.01 3.00

[a] $J_{ab}(gem)$ = 2.5 Hz; J_{ac} = 4.0 Hz; J_{bc} = 7.5 Hz; J_{cd} = 6.5 Hz. Integration accuracy ±2%.

The data in Tables I–III are entirely consistent with the intermediate V and do not allow for the possibility of a concerted migration of only that hydrogen transoid to the departing nitrogen as in VI. McGreer[9] has recently demonstrated such a participation in the pyrolysis of 3-carbomethoxy-4-alkylpyrazolines, thus demonstrating the existence of a different mechanism when electron-withdrawing groups are present on C_3.



VI

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Received April 6, 1967

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(6) R. J. Crawford, A. Mishra, and R. J. Dummel, *J. Am. Chem. Soc.*, **88**, 3959 (1966).

(7) Rate constants for III and IV compared with I yield k_H/k_D values of 1.07 ± 0.04 and 1.05 ± 0.04, respectively.[1]

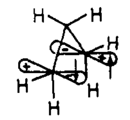
(8) A 20-ft silver nitrate and propanediol column was used to separate the methylcyclopropane and *trans*-2-butene from the *cis*-2-butene and 1-butene. A 20-ft dimethylsulfolane on Chromosorb WAW column, cooled to −25°, was used to separate the latter two hydrocarbons.

(9) D. E. McGreer and W-S. Wu, *Can. J. Chem.*, **45**, 461 (1967).

Thermolysis of *cis*- and *trans*-3,4-Dimethyl-1-pyrazoline

Sir:

Previous studies of the thermolysis of alkyl- and vinyl-1-pyrazolines have demonstrated the existence of a nitrogen-free intermediate which is capable of conversion to alkenes and cyclopropanes.[1] This intermediate, most probably an antisymmetric singlet having the geometry I,[2] has the same stoichiometry and spin state as a possible adduct of singlet methylene to ethylene.[3]



I

The most thoroughly studied example of singlet methylene addition to an olefin is that using *cis*- and *trans*-2-butene as a substrate.[4] This has lead to the speculation that the two carbon–carbon bonds are formed

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(1) (a) R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3963 (1966); (b) R. J. Crawford and G. Erickson, *ibid.*, **89**, 3907 (1967); (c) R. J. Crawford and D. M. Cameron, *Can. J. Chem.*, **45**, 691 (1967).

(2) R. Hoffmann, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Paper 109K.

(3) For an excellent discussion of this problem see (a) P. Gasper and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, Inc., New York, N. Y., 1964, p 235; and (b) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

(4) F. A. L. Anet, R. F. W. Bader, and A. Van der Auwera, *J. Am. Chem. Soc.*, **82**, 3217 (1960); H. M. Frey, *ibid.*, **82**, 5947 (1960); D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962); R. F. W. Bader and J. I. Generosa, *ibid.*, **43**, 1631 (1965).